

# PATENT SPECIFICATION

NO DRAWINGS

906.412



Date of Application and filing Complete Specification: Dec. 18, 1959.

No. 43089/59.

Application made in France (No. 789,341) on March 13, 1959.

Complete Specification Published: Sept. 19, 1962.

12

Index at acceptance:—Classes 2(6), P4D(3B1:8), P4K9, P4P(1A:1E1:1E6:4C:5:6A:6C:6D), P7D(2A1:8), P7K9, P7P(1A:1E1:1E6:4C:6A:6C:6D), P8D(2B2:3A:8), P8K9, P8P(1A:1E1:1E6:4C:6A:6C:6D), P9D(1A1:1B1:8), P9K(4:7:8:9), P9P(1A:1E1:1E6:4C:5:6A:6C:6D); and 91, F1.

International Classification:—C08f. C10n.

## COMPLETE SPECIFICATION

### Additives for Lubricating Oils

We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organized and existing under the laws of the State of Delaware, United States of America, of Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for preparing additives for lubricating oils.

It is a well known process in the art to add to lubricating oils intended for lubricating internal combustion engines, with a view to improving their properties, various addition products, which latter are particularly useful for making the oils detergent, for raising their viscosity index, and for lowering their pour point.

Use is made for this purpose of products obtained either by:—

(I) polymerisation of (1) di-esters of  $\alpha,\beta$ -unsaturated dicarboxylic acids and aliphatic, alicyclic or aromatic alcohols, wherein the alcohols may carry such substituent groups as alkoxy, thioalkoxy, halogen,  $\text{NO}_2$ ,  $\text{HSO}_3$ , CN and other groups; (2) monoesters of  $\alpha,\beta$ -unsaturated dicarboxylic acids and alkoxy-substituted, aliphatic, alicyclic or aromatic alcohols; or (3) amino-substituted esters of the acids and alcohols mentioned above; or by:—

(II) copolymerisation of the above esters with further polymerisable organic compounds, such as, (1) esters of unsaturated alcohols, such as vinyl esters, e.g. vinyl acetate; (2) esters of alcohols carrying no alkoxy substituent groups and  $\alpha,\beta$ -unsaturated monocarboxylic acids, such as methacrylates; (3) aromatic hydrocarbons having ethylene side chains, such as styrene; (4) unsaturated nitriles, e.g. acrylonitrile; or (5) anhydrides of  $\alpha,\beta$ -unsaturated dicarboxylic acids, e.g. maleic

anhydride.

However, the polymers or copolymers thus obtained do not as a rule possess to the same degree the properties of improving the viscosity index and of lowering the pour point.

It is also well known that the polymers or copolymers of heavy alcohols are particularly effective pour depressants while polymers or copolymers of esters of light alcohols are particularly effective viscosity index improvers. Esters of heavy alcohols are herein defined as esters of alcohols having at least 12 carbon atoms, or esters of a mixture of several alcohols, some of which may have less than 12 carbon atoms, provided that the mean molecular weight of this mixture corresponds to that of an alcohol having at least 12 carbon atoms. Nevertheless, esters of high-molecular weight, having more than 18 carbon atoms, possess the drawback of yielding highly viscous polymers, which raise the viscosity of the oil considerably. It is preferred, therefore, to use esters of  $\text{C}_{12}$ — $\text{C}_{18}$  alcohols or esters of a mixture of alcohols whose mean molecular weight corresponds to that of  $\text{C}_{12}$ — $\text{C}_{18}$  alcohols.

Esters of light alcohols are herein defined as esters of alcohols having less than 12 carbon atoms or esters of a mixture of several alcohols, some of which may have 12 or more carbon atoms, provided that the mean molecular weight of this mixture corresponds to that of an alcohol having less than 12 carbon atoms. Nevertheless, esters of alcohols having less than 3 carbon atoms have the drawback of yielding polymers that are very little soluble in the oils. It is preferred therefore to use esters of alcohols having from 3—11, particularly 7—11 carbon atoms or esters of a mixture of several alcohols whose mean molecular weight corresponds to that of an alcohol having from 7—11 carbon atoms.

To obtain an additive capable of improving both the viscosity index and the pour point

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of lubricating oils, a solution would therefore appear to consist in the polymerisation or the copolymerisation of a charge comprising a mixture of esters of heavy alcohols and esters of light alcohols, in the presence or otherwise of a further polymerisable organic compound.

5 This solution obviously produces a certain result, but when the proportion in the mixture of esters of heavy alcohols is increased to lower the pour point, it is found that the efficiency of the copolymer as regards the viscosity index decreases.

10 According to the present invention, a process for preparing oil-soluble copolymers of one or more esters (A) of an  $\alpha,\beta$ -unsaturated dicarboxylic acid and a heavy alcohol (as hereinbefore defined) and one or more esters (B) of such an acid and a light alcohol (as hereinbefore defined) consists in carrying out the copolymerisation in two stages, the charge to the first stage comprising a mixture of the two types of ester (A) and (B) and the charge to the second stage comprising one only of the types of ester (A) or (B) in the absence of the other type of ester.

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25 Preferably the copolymerisation in both stages is carried out in the presence of a further copolymerisable compound, in particular vinyl acetate.

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Copolymers are obtained by the process of the invention which have very great efficiency in lowering the pour point and improving the viscosity index of lubricating oils.

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According to a further feature of the invention, copolymerisation may be carried out in the presence of the polar monomer monobutyl maleate, which may be added at the first stage.

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According to a further feature of the invention, a diluent oil may be used during the polymerisation, and this is preferably added during the second stage of the process.

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The process of polymerisation according to the invention makes it possible to obtain essentially:—

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1. Macro-molecules of esters of heavy alcohols, formed during the first stage and characterised by their aptitude to lower the pour point of lubricating oils and by their good solubility in these oils.

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2. Macro-molecules containing a high proportion of esters of light alcohols and a low proportion of esters of heavy alcohols, derived from copolymerisation, during the 2nd stage, esters of light alcohols with esters of heavy alcohols that have not taken part in the polymerisation of the 1st stage, the said macro-molecules being characterised by their ability to improve the viscosity index of lubricating oils, and owing to the presence of esters of heavy alcohols, by their good solubility in these oils.

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3. Mixed macro-molecules of esters of heavy alcohols and esters of light alcohols where the molecules of esters of heavy alcohols

are grouped at the start of the chain and the molecules of esters of light alcohols at the end of the chain, derived from the continuation, during the 2nd stage, of the incomplete polymerisation of the 1st stage, the said macro-molecules being characterised by double activity in respect of the viscosity and the pour point of the lubricating oils, and by good solubility in the latter.

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By copolymerisation with a further polymerisable organic compound there are also obtained three types of macro-molecules, defined above, containing molecules of the further polymerisable compound used. It should be pointed out that the latter can be added equally well during the first or during the second stage.

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Finally, the mixture of macro-molecules obtained by the process of polymerisation in two stages according to the invention, is endowed with good ability to lower the pour point and to improve the viscosity index of the lubricating oils and with good solubility in the latter, and indeed with increased efficiency compared with that of mixtures of macro-molecules derived either from a polymerisation process in a single stage, or from a process of separate polymerisations.

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In the charge to be copolymerised in the first stage the percentage (by weight in relation to the total weight of the esters (A) and (B) in the charge to the first stage) of esters of heavy alcohols is for preference at least 25% and preferably between 60 and 40%, and that of light esters is correspondingly for preference less than 75% and preferably between 40 and 60%. The heavier the alcohols, the better possible it is to increase the amount of the light alcohol ester in to the first stage.

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The polymers and copolymers obtained according to the invention can likewise have detergent properties, especially when they are prepared from esters of alkoxy-substituted alcohols or from amino-substituted esters.

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The polymers and copolymers according to the invention must, for this purpose, be used in proportions ranging for preference from 0.01 to 20%, and better still, from 1 to 10% by weight of the lubricating composition.

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The process according to the invention can be used whatever the method of polymerisation or copolymerisation employed. It is possible to make use of the effects of heat and pressure, of catalysts, such as light, oxygen, ozone, boron fluoride, aluminium chloride and for preference peroxides, such as benzoyl peroxide.

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The reaction is generally accomplished in a space of time that may range from 2 to 100 hours, according to the catalyst and the conditions of temperature which may vary from 50 to 150°C. It is also possible to operate in the presence of inert solvents such as petrol, a light lubricating oil, and chloroform, for the purpose of controlling the rate of the reaction

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2. 2nd stage - Polymer  
1. 1st stage - R  
2. 2nd stage - A and B  
R

or the molecular weight of the product, but the use of such solvents is not compulsory.

The following examples will better show the scope and importance of the invention.

#### EXAMPLE I

Two copolymers were prepared from charges having the same total composition, by conducting copolymerisation first in one stage and then in two.

Composition of charge to be copolymerised (% by weight)	A1 Copolymerisation in one stage	B1 Copolymerisation in two stages	
	Total charge	Initial Charge	Additional Charge
C <sub>8</sub> alcohol fumarate	50	10	40
C <sub>18</sub> —C <sub>18</sub> Alcohol fumarate	10	10	
Vinyl acetate	40	20	20
Benzoyl peroxide	0.5	0.5	0.5
Time of copolymerisation (hours)	4	1½	2½
Characteristics of copolymer obtained after 33% dilution in a paraffin oil of viscosity index 113 & viscosity 5.1 cs at 90°C.			
Viscosity at 99°C. in cs.	690		734

The following table shows the compared effects of these two copolymers from the point of view of raising the viscosity index and lowering the pour point, when they are

added to a paraffin oil having viscosity index 113 and viscosity index 12 centistokes at 37.8°C.

% Copolymer (active product in oil)	Viscosity Index		Pour Point °C.	
	A1	B1	A1	B1
0.5	113		-9	
0.5	—	—	-9	-15
1	139	142	-15	-21
2	148	151	-15	-27

#### EXAMPLE II

B2 were prepared from charges having the same total composition, by effecting copolymerisation in one and then two stages.

20 As in Example I, two copolymers A2 and

Composition of charge to be copolymerised (% by weight)	A2 Copolymerisation in one stage	B2 Copolymerisation in two stages	
	Total charge	Initial Charge	Additional Charge
C <sub>8</sub> alcohol fumarate	45	15	30
C <sub>16</sub> —C <sub>18</sub> alcohol fumarate	15	15	—
Vinyl acetate	40	10	30
Benzoyl peroxide	0.5	0.5	0.5
Time of copolymerisation (hours)	4	2	2
Characteristics of copolymer obtained after 33% dilution in a paraffin oil of viscosity index 113 & viscosity 5.1 cs at 99°C.			
Viscosity at 99°C. in cs.	605		560

The following table shows the compared effects of these two copolymers when they are added to the same basic paraffin oil as in Example I.

% copolymer (Active product in oil)	Viscosity Index		Pour Point °C.	
	A2	B2	A2	B2
0		113		-9
0.5			-21	-27
1	140	141.5		
2	148	151	-21	-33

#### EXAMPLE III

As in the previous examples, two copolymers

A3 and B3 were prepared from charges having the same total composition, by conducting copolymerisation in one stage and then in two.

Composition of charge to be copolymerised (% by weight)	A3 Copolymerisation one stage	B3 Copolymerisation in two stages	
	Total charge	Initial Charge	Additional Charge
C <sub>8</sub> alcohol fumarate	40	15	25
C <sub>16</sub> —C <sub>18</sub>	15	15	—
Maleofumarate of C <sub>8</sub> alcohol, to which alcohol were added 3 mols. ethylene oxide per mol. of alcohol	5	—	5
Vinyl acetate	40	10	30
Benzoyl peroxide	0.5	0.5	
Time of copolymerisation (hours)	4	2	2
Characteristics of copolymer obtained after 33% dilution in a paraffin oil of viscosity index 113 & viscosity 5.1 cs at 99°C.			
Viscosity at 99°C. in cs.	730		680

The following table shows the compared effects of these two copolymers when added to the same basic paraffin oil as in Example I.

% copolymer (Active product in oil)	Viscosity Index		Pour Point °C.	
	A3	B3	A3	B3
0	113		-9	
0.5	128	129	-18	-21
1	139	140	-21	-30
2	151	152	-21	-33
4	153	156	-21	-33

In our U.K. Patent Specification 806,906 there is described and claimed an oil-soluble copolymer of vinyl acetate and a dialkyl fumarate mixture wherein said dialkyl fumarate mixture contains an average of 9 to 11 carbon atoms per alkyl group and wherein said mixture consists essentially of (1) dialkyl fumarates having 8 carbon atoms in a branched chain in each alkyl group and (2) dialkyl fumarates having 14 to 18 carbon atoms in a straight chain in each alkyl group.

#### WHAT WE CLAIM IS:—

1. A process for preparing oil-soluble copolymers of one or more esters (A) of an  $\alpha,\beta$ -unsaturated dicarboxylic acid and a heavy alcohol (as hereinbefore defined) and one or more esters (B) of such an acid and a

light alcohol (as hereinbefore defined) which consists in carrying out the copolymerisation in two stages, the charge to the first stage comprising a mixture of the two types of ester (A) and (B) and the charge to the second stage comprising one only of the types of ester (A) or (B) in the absence of the other type of ester.

2. A process as claimed in claim 1, wherein one or more of the esters are diesters of the said acids.

3. A process as claimed in claim 1 or claim 2, wherein the alcohols carry an alkoxy, thioalkoxy, halogen, NO<sub>2</sub>, HSO<sub>3</sub>, or CN substituent group.

4. A process as claimed in claim 1 or claim 3, wherein one or more of the esters are monoesters of the said acids and alkoxy-substituted

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alcohols.

5. A process as claimed in any preceding claim, wherein the esters are amino-substituted.
- 5 6. A process as claimed in any preceding claim, wherein the mixture of the two types of ester (A) and (B) in the charge to the first stage consists of at least 25% by weight of esters (A) and correspondingly not more than
- 10 75% by weight of esters (B).
7. A process as claimed in claim 6, wherein the said mixture consists of from 40 to 60% by weight of esters (A) and correspondingly from 60 to 40% by weight of esters (B).
- 15 8. A process as claimed in any of claims 1 to 7, wherein the copolymerisation in both stages is carried out in the presence of a further polymerisable compound.
- 20 9. A process as claimed in claim 8, wherein the further polymerisable compound is vinyl acetate.
10. A process as claimed in any preceding

claim, wherein the copolymerisation is carried out in the presence of monobutyl maleate added at the first stage.

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11. A process as claimed in any preceding claim, wherein a diluent oil is added during the second stage.

12. A process as claimed in claim 1, substantially as hereinbefore described in any of the Examples.

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13. An oil-soluble copolymer of esters of  $\alpha,\beta$ -unsaturated dicarboxylic acids and heavy and light alcohols (as hereinbefore defined) when produced by a process as claimed in any preceding claim.

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14. A lubricating composition comprising a lubricating oil and from 0.01 to 20% by weight of a copolymer as claimed in claim 13.

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